

(12) **UK Patent Application** (19) **GB** (11) **2 152 082 A**

(43) Application published 31 Jul 1985

(21) Application No **8431271**

(22) Date of filing **12 Dec 1984**

(30) Priority data  
(31) **565492** (32) **27 Dec 1983** (33) **US**

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(51) INT CL<sup>4</sup>  
**C23F 15/00**

(52) Domestic classification  
**C7U 3 7A 7J  
U1S 3013 C7U**

(56) Documents cited

<b>GB A 2081747</b>	<b>GB 0559591</b>	<b>US 3754903</b>
<b>GB A 2075556</b>	<b>GB 0513276</b>	<b>US 3754902</b>
<b>GB 1135313</b>	<b>GB 0462380</b>	<b>US 3676085</b>
<b>GB 0662333</b>	<b>US 3928026</b>	<b>US 3542530</b>

(58) Field of search  
**C7U**

(54) **Enhancement of superalloy resistance to environmental degradation**

(57) Method for improving the oxidation and hot corrosion resistance of superalloy articles, of the type which contain oxygen active elements is disclosed. The method comprise exposing a superalloy article containing at least about 3% aluminium, at least about 5% Cr, from about .01 to about 9% of at least one element selected from Y, Hf, La, Ce, Sc, Mg, Mn and Misch metal 6 a clean oxidizing environment at a temperature of about 649°C to about 1093°C for about 4 to about 40 hours to develop a protective alumina base surface layer.

The articles have their surfaces prepared by cleaning and are then preoxidized in a clean controlled oxidizing environment at an elevated temperature. This treatment ensures that the oxide film which forms is dense, adherent, protective and comprised largely of alumina.

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## SPECIFICATION

**Enhancement of superalloy resistance to environmental degradation**

## 5 Technical Field

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This invention relates to the improvement of the resistance of superalloy materials to environmental attack especially high temperature oxidation and hot corrosion.

## Background Art

- 10 Nickel base superalloys are widely used in applications where strength is important at elevated temperatures. In most such applications there is a concurrent requirement that the materials be resistant to oxidation and hot corrosion. Nickel base superalloys consist of a gamma matrix (nickel solid solution) containing a strengthening phase, gamma prime, ( $\text{Ni}_3\text{Al}$  based). In addition to participating in the formation of the strengthening gamma prime phase the aluminum (typically present in amounts of about 3–7%) in nickel base superalloys contributes materially to their resistance to oxidation and corrosion by forming an alumina based layer on the exterior surface of superalloy articles upon exposure to oxidizing conditions. It is necessary to have a certain amount of chromium present in order to reliably form a true alumina layer with the amounts of aluminum that are usually employed in superalloys. Chromium levels in excess of about 5% appear to be necessary.

- 20 Once formed, the alumina layer protects the underlying superalloy from oxidation corrosion by inhibiting the diffusion oxygen into the substrate and by inhibiting the diffusion of the substrate materials to the outer surface where they would contact the reactive environment. A characteristic of surface layers which form by environmental reaction is that they usually follow a parabolic growth pattern; the initial rate of formation of the film on a bare surface is high but the rate tapers off in a parabolic fashion as the thickness of the layer increases and the reaction of the substrate and the environment is thereby reduced (the growth rate is inversely proportional to the oxide thickness).

- 25 There appear to be two major mechanisms by which the protective properties of alumina layers are rendered ineffective in service. When the alumina layer contains impurities, the perfection and density of the surface film are reduced and the diffusion rate of oxygen into the substrate and substrate materials to the surface increases. The second failure mechanism is the spallation of the alumina surface layer. Spallation is usually caused by thermal expansion of the article. Since the metallic substrate has a higher coefficient of thermal expansion than the alumina layer, the surface layer is put in tension as the oxidized article is heated to a temperature above the temperature at which the oxide film was formed (of course, upon cooling the reverse effect occurs).

- 30 The problem of improving surface layer performance has been addressed by modifying the substrate composition to minimize the tendency to form oxides other than alumina and the tendency towards spallation has been addressed by the incorporation of certain so-called oxygen active elements into the underlying substrate.

- 35 In connection with the development of certain protective coatings it was found that the inclusion in such coatings of oxygen active elements such as yttrium, lanthanum, scandium, hafnium, silicon, magnesium and the like reduced the spallation of the alumina layer substantially. These coating are discussed in U.S. Patent Nos. 3,542,530, 3,676,085, 3,754,903 and 3,928,026. U.S. Patent No. 3,754,902 describes a structural alloy which includes Y for the purpose of improving oxidation performance.

- 40 The copending application entitled "Enhanced Oxidation Resistance for Superalloy Articles Through Additions of Yttrium and Hafnium", U.S. Serial No. (F-4974), filed on even date herewith describes a synergistic effect observed in superalloy substrates when controlled combinations of yttrium and hafnium are present.

## Disclosure of Invention

- 45 According to the present invention the environmental resistance of superalloy substrates of the type which form protective alumina surface layers and which contain oxygen active elements is substantially improved by preoxidizing the superalloy surface in a controlled clean oxidizing environment prior to exposing the materials to service environments. It is theorized that this preoxidizing treatment insures the formation of a highly perfect and therefore more highly protective alumina surface layer and that the presence of the oxygen active elements thereafter serves to stabilize this perfect surface layer and minimizes spallation during service exposure.

- 50 The invention results will be discussed with reference to test results of a series of alloys whose composition is set forth in Table I. In Table I the alloys referred to as Prior Art A and Prior Art B are commercial superalloys which are outside of the scope of the present invention by virtue of the absence of oxygen active elements in the ranges required by the invention. These alloys however do form protective alumina layers because they contain aluminum and chromium in the

requisite amounts. The other alloys in Table I are representative of those to which the present invention can be applied; these alloys have a wide variety of basic compositions and all contain small amounts of both yttrium and hafnium.

5 Samples of these alloys were tested in a hot corrosion test at 899°C using a ducted burner rig in which controlled amounts of sulphur dioxide were added to simulate surface environment. 5  
Samples were tested to failure, in both the as machined condition and after preoxidizing treatment for 24 hours at 1038°C in air.

TABLE I

<u>Alloy ID</u>	<u>Ni</u>	<u>Cr</u>	<u>Al</u>	<u>W</u>	<u>Ta</u>	<u>Nb</u>	<u>Mo</u>	<u>Re</u>	<u>Ti</u>	<u>Co</u>	<u>Y</u>	<u>Hf</u>	<u>Others*</u>
2-88	Bal	12.0	7.0	9.0	1.5	--	1.0	--	--	--	0.051	0.17	--
2-108	Bal	11.9	6.9	8.0	--	1.6	--	--	--	--	0.027	0.17	--
2-153	Bal	8.6	7.0	8.0	3	--	1.0	--	--	--	0.038	0.18	--
2-155	Bal	12.0	7.0	7.0	3	--	2.0	--	--	--	0.036	0.18	--
2-204	Bal	12.0	6.5	5.0	3	--	--	3	--	--	0.043	0.16	--
2-205	Bal	12.0	6.5	4	5	--	--	3	--	--	0.045	0.19	--
2-203	Bal	3.0	6.8	6	3	--	4.0	3	--	--	0.04	0.18	--
597	Bal	8.9	6.7	9.4	3.1	--	1.0	--	--	--	~0.1	~0.2	--
Prior Art A	Bal	9.0	5.0	12.5	--	1.0	--	--	2.0	10.0	--	--	C, B, Zr
Prior Art B	Bal	10.0	5.0	4.0	12.0	--	--	--	1.5	5.0	--	--	--

\*Minor elements

Note: Weight percent

The results are shown in Table II and it can be seen that the preoxidizing step is effective in increasing the life of the invention specimens by a factor of at least two or three. This is a surprising and unexpected result and is attributed to the formation of a more perfect, more dense, more pure alumina film during the preoxidation procedure and the retention of this film by virtue of the presence in the material of the oxygen active elements.

The results of corrosion testing for 100 hours at 899°C are demonstrated in Figs. 1, 2 and 3. These figures are photomicrographs taken at a magnification of 200X of alloys 108, Prior Art A and Prior Art B. The alloy 108 composition is not dissimilar from the compositions of the Prior Art A and Prior Art B except of course for the inclusion of the yttrium and hafnium in the invention amounts. Looking now at Figs. 1, 2 and 3, it can be seen that the invention alloy after a similar period of testing under identical conditions displayed a depth of attack approximately one-tenth of that displayed by alloy Prior Art B and about one-thirtieth of that displayed by the Prior Art A sample.

These micrographs illustrate the magnitude of the improvement obtained by applying the invention preoxidation treatment to a particular alloy which satisfies the criteria previous set forth.

TABLE II

RESULTS OF HOT CORROSION BURNER TESTS

<u>Alloy ID</u>	<u>Series 1 As Ground</u>	<u>Series 2 Pre-Oxidized*</u>
2-88	--	216
2-108	120	216
2-153	--	800 Stop Test
2-155	192	800 Stop Test
2-204	--	800 Stop Test
2-205	--	800 Stop Test
597	180	288
2-203	--	216
Prior Art A	96	96
Prior Art B	96	96

\*Pre-Oxidized 24 Hours at 1038°C.

Prior to Testing -- Duplicate Tests

The promising results produced by the present invention open the possibility of the use of superalloys in the uncoated condition in certain engine applications. This has not only economic implications but could result in improvements in other properties. Consider for example Fig. 4 which illustrates the thermomechanical fatigue behavior of a typical nickel base superalloy tested in the single crystal condition (Prior Art B alloy). The vertical axis shows the percent strain while the horizontal axis shows the number of cycles required to cause failure by cracking over a particular strain range. It can be seen that the overlay coating adversely affects the thermomechanical fatigue behavior. For example for a part cycled  $\pm .6\%$  true strain, the coated articles

failed at about 5000 cycles while the uncoated articles failed at about 15,000 cycles. Thus for applications where thermomechanical fatigue is a limiting factor the use of the present invention process may offer a substantial benefit.

Another application for the present invention is for the elimination of oxidation and corrosion in internal air cooling passages. Most turbine engines employ air cooling passages. Most turbine engines employ air cooled turbine blades in which air is circulated through passages in the blades in order to keep the outer temperature of the blades within reasonable limits. Because the surfaces of these interior cooling passages can reach a relatively high temperature, it has been a common practice to coat the internal passages using a protective coating (usually) of the aluminate type. The coating process and the necessary destructive inspection of coated samples in order to assure quality control add to the cost of producing the air cooled turbine blades. The present invention makes it quite likely that this internal coating process could be eliminated. Other features and advantages will be apparent from the specification and claims and from the accompanying drawings which illustrate an embodiment of the invention.

#### Brief Description of Drawings

Figure 1 is a photomicrograph of a cross section of alloy 108 after oxidation testing;

Figure 2 is a photomicrograph of a cross section of prior art A alloy after oxidation testing;

Figure 3 is a photomicrograph of a cross section of prior art B alloy after oxidation testing;

and Figure 4 is a plot showing thermomechanical fatigue behavior of the invention processed alloys and a prior art alloy.

#### Best Mode for Carrying Out the Invention

The present invention is applicable to nickel base superalloys of the type which form an alumina surface layer. In order to form an alumina surface layer at least about 3% aluminum must be present in the alloy in combination with about 5% chromium. A further requirement of the alloy is that at least one oxygen active element of the group consisting of yttrium, hafnium, lanthanum, cerium, scandium, magnesium, manganese and misch metal be present in an amount from about .01 to about .9%. Preferably at least two of these elements are present in the total range of from .05 to .5%. Most preferably, based on results to date, the elements are yttrium and from .3 to .8% for hafnium. The method of fabrication of the material is unimportant, i.e., conventional polycrystalline casting, directional solidification, single crystal, or powder metallurgy techniques may be employed so long as the oxygen active element is uniformly distributed throughout the material, especially in regions adjacent to surfaces where oxidation and corrosion protection is required.

The alloy should be cleaned to remove all surface oxides and dirt, grease, oil and the like. The article should then be heat treated in a clean environment at a temperature of from about 649°C to about 1093°C for a period of from about 4 to about 40 hours. Oxidation at lower temperature ranges will require longer time than oxidation at higher temperatures in order to produce an equivalent thickness oxide layer.

Oxidation may be performed in air or in another oxidizing environment such as a mixture of oxygen and some other inert gas. As previously indicated we have obtained particularly successful results using a time of 24 hours and a temperature of 1038°C but it is apparent that other compositions may require other times and temperatures to produce optimum results.

It should be understood that the invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the spirit and scope of this novel concept as defined by the following claims.

#### CLAIMS

1. A method of improving the oxidation resistance of a superalloy article containing at least about 3% aluminum, at least about 5% Cr, from about .01 to about .9% of at least one element selected from the group consisting of Y, Hf, La, Ce, Sc, Mg, Mn and Misch metal, said article having a clean oxide free surface, which comprises:

exposing the article to a clean oxidizing environment at a temperature of from about 649°C to about 1093°C for from about 4 to about 40 hours to develop a protective alumina base surface layer of high perfection.

2. A method as in claim 1 in which the alloy contains at least two elements selected from the group consisting of Y, Hf, La, Ce, Sc, Mg, Mn and Misch metal.

3. A method as in claim 1 in which Hf and Y are present in the alloy in a total amount of about .01 to about .5%.

4. A method as in claim 3 in which hafnium is present in an amount from about .3 to about .8% and Y is present in an amount from about .01 to about .09%.

5. The article produced according to the method of claims 1-4.

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Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1985, 4235  
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained

FIG. 3

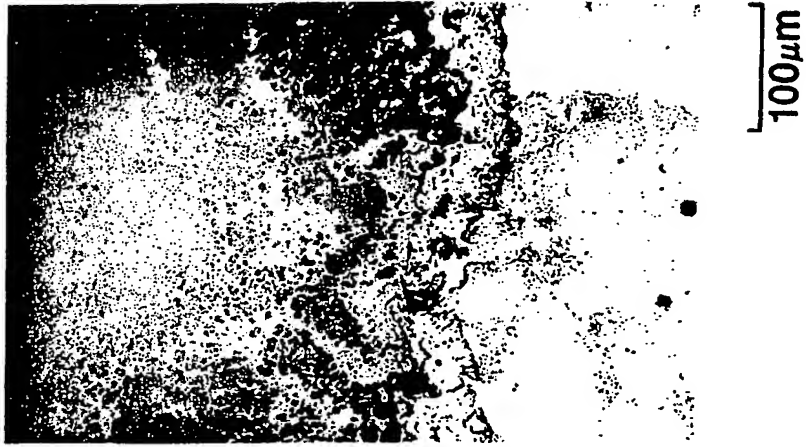


FIG. 2

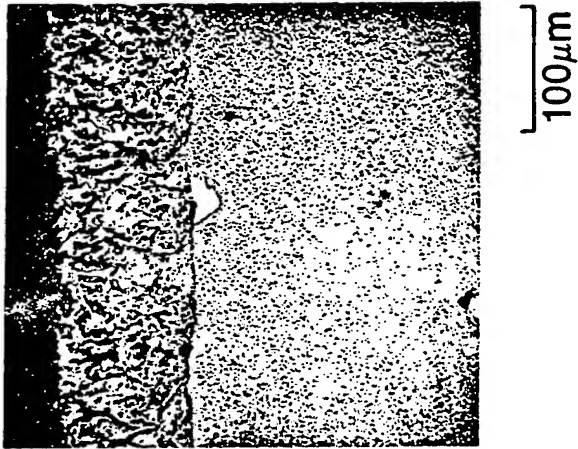
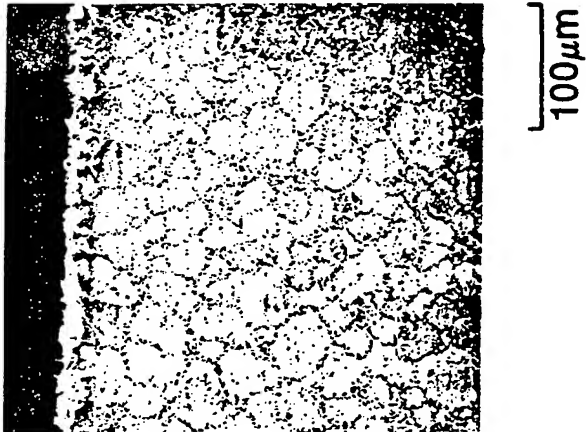


FIG. 1





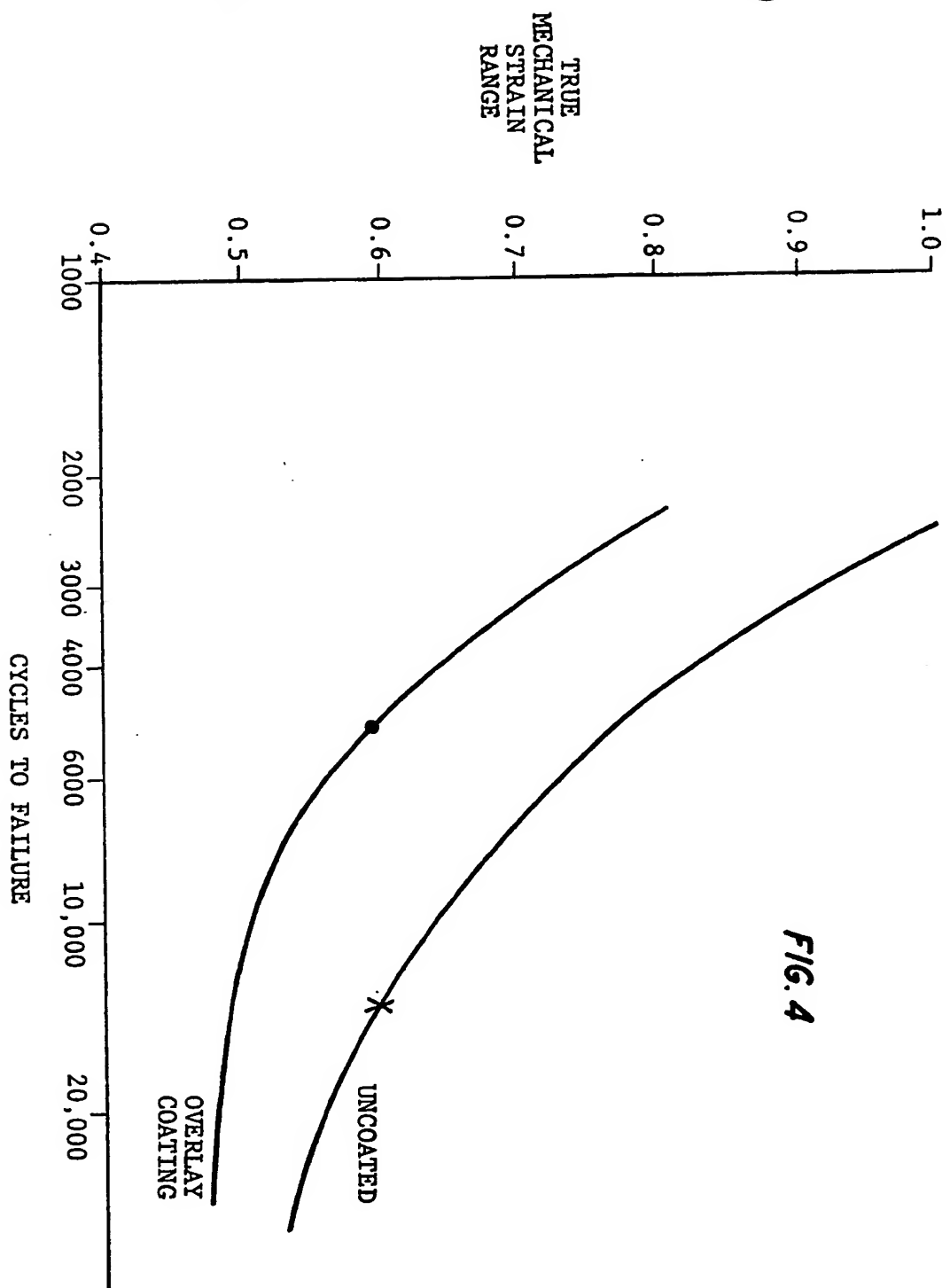


FIG. 4

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